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(54) Title: SCHIFF BASE DERIVATIVES OF RUTHENIUM AND OSMIUM OLEFIN METATHESIS CATALYSTS			
(57) Abstract <p>The present invention generally relates to ruthenium and osmium carbene catalysts for use in olefin metathesis reactions. More particularly, the present invention relates to Schiff base derivatives of ruthenium and osmium carbene catalysts and methods for making the same. The inventive catalyst are generally prepared by the treatment of unmodified catalysts with the salts of the desired Schiff base ligands, in which an anionic and a neutral electron donating ligands of the unmodified catalysts are simultaneously replaced. The Schiff base derivatives of the ruthenium and osmium carbene catalysts show unexpectedly improved thermal stability while maintaining high metathesis activity, even in polar protic solvents. Although the inventive catalysts may be used in all metathesis reactions, use of these catalysts for ring-closing metathesis ("RCM") reactions is particularly preferred.</p>			

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SCHIFF BASE DERIVATIVES OF RUTHENIUM AND OSMIUM OLEFIN METATHESIS CATALYSTS

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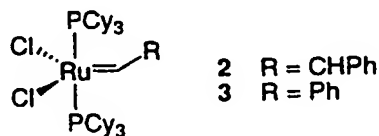
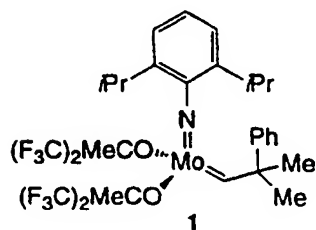
BACKGROUND

A large number of catalyst systems that can initiate olefin have been introduced. However, most early work in olefin was done using ill-defined multi-component catalyst systems. It is only in recent years that well-defined single component metal carbene complexes have been prepared and extensively utilized in olefin metathesis.

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With the advent of efficient catalyst systems, olefin metathesis has emerged as a powerful tool for the formation of C-C bonds in chemistry. Of importance among the well-defined catalyst systems is the alkoxy imido molybdenum system 1 developed by Schrock and co-workers and the benzylidene ruthenium carbene complexes 2-3 developed by Grubbs and co-workers.

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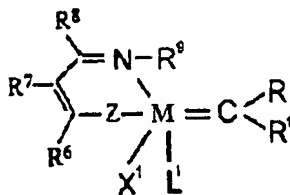


In particular, the ruthenium carbene catalyst systems have drawn a lot of attention, not only because they exhibit high reactivity for a variety of metathesis processes under mild conditions, but also because of their remarkable tolerance of many organic functional groups. However, although these ruthenium carbene catalysts (particularly complexes 2 and 3) have been used in diverse olefin metathesis reactions with remarkable success, further improvements such as better thermal stability, high activity in polar protic solvents, and chiral and cis/trans selectivity, are required to more fully exploit their commercial potential.

SUMMARY OF THE INVENTION

The present invention generally relates to ruthenium and osmium carbene catalysts for use in olefin metathesis reactions. More particularly, the present invention relates to Schiff base derivatives of ruthenium and osmium carbene catalysts and methods for making the same.

The Schiff base catalysts are of the general formula



wherein:

M is ruthenium or osmium;

X¹ is an anionic ligand;

L¹ is a neutral electron donor;

R and R¹ are each hydrogen or a substituent selected from the group

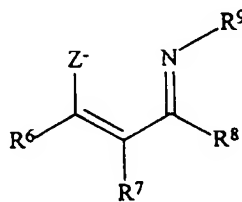
consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties
 5 selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

Z is selected from the group consisting of oxygen, sulfur, -NR¹⁰, and -PR¹⁰, and

R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, each non-hydrogen group
 10 optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

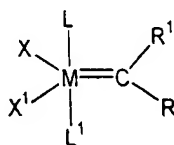
wherein X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic
 15 acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

The Schiff base ligands are prepared by the condensation of comprising contacting a salt of a Schiff base having the formula



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with compound having the formula



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wherein

M, X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ are as previously described;

X is an anionic ligand; and,

L is a neutral electron donor.

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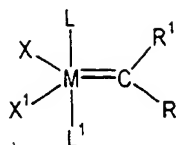
The Schiff base catalysts of the present invention show unexpectedly improved thermal stability over unmodified ruthenium and osmium catalysts, and maintain high metathesis activity even in polar protic solvents. Although the inventive catalysts may be used in all metathesis reactions, ring-closing
10 metathesis ("RCM") reactions are particularly preferred since it is favored over other competing reactions at higher temperatures. In addition, because they provide convenient routes for including additional functionalities, Schiff base derivatives may play a key role in the design of chiral and/or cis/trans-selective metathesis catalysts.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention generally relates to ruthenium and osmium carbene catalysts for use in olefin metathesis reactions. More particularly, the present
20 invention relates to Schiff base derivatives of ruthenium and osmium carbene catalysts and methods for making the same.

Unmodified ruthenium and osmium carbene complexes have been described in United States Patents Nos. 5,312,940, 5,342,909, 5,728,917, 5,750,815, and
25 5,710,298, all of which are incorporated herein by reference. The ruthenium and osmium carbene complexes disclosed in these all possess metal centers that are formally in the +2 oxidation state, have an electron count of 16, and are penta-coordinated. These catalysts are of the general formula



wherein:

- 5 M is ruthenium or osmium;
 X and X¹ are each independently any anionic ligand;
 L and L¹ are each independently any neutral electron donor ligand;
 R and R¹ are each independently hydrogen or a substituent selected from
 the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀
 10 carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-
 C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀
 alkylsulfinyl. Optionally, each of the R or R¹ substituent group may be
 substituted with one or more moieties selected from the group consisting of C₁-
 C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted
 15 with one or more groups selected from a halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy,
 and phenyl. Moreover, any of the catalyst ligands may further include one or
 more functional groups. Examples of suitable functional groups include but are
 not limited to: hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine,
 imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate,
 20 carbodiimide, carboalkoxy, carbamate, and halogen.

- In preferred embodiments of these catalysts, the R substituent is hydrogen and
 the R¹ substituent is selected from the group consisting C₁-C₂₀ alkyl, C₂-C₂₀
 alkenyl, and aryl. In even more preferred embodiments, the R¹ substituent is
 25 phenyl or vinyl, optionally substituted with one or more moieties selected from
 the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional
 group. In especially preferred embodiments, R¹ is phenyl or vinyl substituted
 with one or more moieties selected from the group consisting of chloride,
 bromide, iodide, fluoride, -NO₂, -NMe₂, methyl, methoxy and phenyl. In the
 30 most preferred embodiments, the R¹ substituent is phenyl.

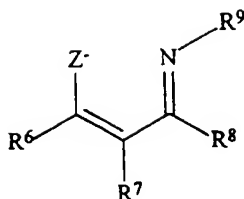
In preferred embodiments of these catalysts, L and L¹ are each independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether. In more preferred
5 embodiments, L and L¹ are each a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl or C₁-C₁₀ alkyl, particularly primary alkyl, secondary alkyl or cycloalkyl. In the most preferred embodiments, L and L¹ ligands are each selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃.

10

In preferred embodiments of these catalysts, X and X¹ are each independently hydrogen, halide, or one of the following groups: C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkyldiketonate, aryldiketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl, or
15 C₁-C₂₀ alkylsulfinyl. Optionally, X and X¹ may be substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from halogen, C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl. In more preferred
20 embodiments, X and X¹ are halide, benzoate, C₁-C₅ carboxylate, C₁-C₅ alkyl, phenoxy, C₁-C₅ alkoxy, C₁-C₅ alkylthio, aryl, and C₁-C₅ alkyl sulfonate. In even more preferred embodiments, X and X¹ are each halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, or trifluoromethanesulfonate. In the most preferred
25 embodiments, X and X¹ are each chloride.

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The catalysts of the present invention are similar to the above catalysts except that X and L are simultaneously substituted with a Schiff base ligand of the general formula



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wherein:

N and Z are coordinated to the metal center, M;

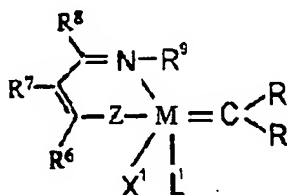
Z is selected from the group consisting of O ("oxygen"), S ("sulfur"),
NR¹⁰, and PR¹⁰; and

10 R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each independently selected from a group
consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl. Each non-hydrogen
group may be optionally substituted with one or more moieties selected from
the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may
each be further substituted with one or more groups selected from halogen, C₁-
15 C₅ alkyl, C₁-C₅ alkoxy, and phenyl.

The term "alkyl" is intended to be inclusive and thus includes all forms of alkyl
moieties such as include primarily, secondary, tertiary, and cyclo alkyl groups.
Illustrative examples of aryl and heteroaryl moieties include but are not limited
20 to: anthracyl, adamantyl, furyl, imidazolyl, isoquinolyl, phenyl, naphthyl,
phenanthracyl, pyridyl, pyrimidyl, pyrrol, and quinolyl. Moreover, adjacent R
groups, R⁶ and R⁷, may together form a substituted or unsubstituted cyclic group
(*i.e.* aryl, cycloalkyl, or heteroaryl). Each of R⁶, R⁷, R⁸, R⁹, and R¹⁰ may be
optionally substituted with one or more moieties selected from the group
25 consisting of C₁-C₁₀ alkyl, C₁-C₁₀ and aryl. In addition, the Schiff base ligand
may include one or more functional groups. Examples of suitable functional
groups include but are not limited to: hydroxyl, thiol, thioether, ketone,
aldehyde, ester, ether, amine, amide, nitro, carboxylic acid, disulfide, carbonate,
isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

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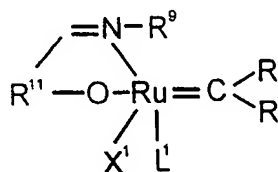
The resulting catalysts are of the general formula



wherein M, R, R¹, R⁶, R⁷, R⁸, R⁹, Z, X¹, and L¹ are as previously defined.

- 5 In preferred embodiments: M is ruthenium; R is hydrogen; R¹ is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl; L¹ is a phosphine of the formula PR³R⁴R⁵ wherein R³, R⁴, and R⁵ are each selected from the group consisting of aryl, C₁-C₁₀ primary alkyl, secondary alkyl, and cycloalkyl; and, X¹ is selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂,
 10 (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and, trifluoromethanesulfonate.

In more preferred embodiments, the inventive catalysts are of the general formula



- 20 wherein R, R¹, R⁹, X¹, and L¹ are as previously defined, and R¹¹ is an aryl or heteroaryl group, optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl. With reference to the general formula for the Schiff base catalyst derivative, M is ruthenium; Z is oxygen; R⁸ is hydrogen, and R¹¹ is an aryl or heteroaryl group that is formed by
 25 the joining of R⁶ and R⁷.

In even more preferred embodiments of the Schiff base complexes:

X¹ is chloride;

L¹ is selected from the group consisting of -P(cyclohexyl)₃,
 5 -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

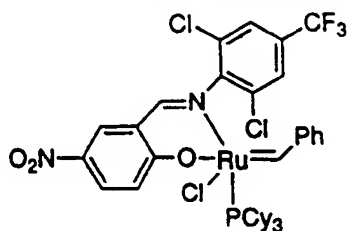
R is hydrogen;

R¹ is phenyl or vinyl, optionally substituted with one or more moieties
 selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl;

R⁹ is an aryl or heteroaryl substituted with at least one moiety off its
 10 aromatic ring; and

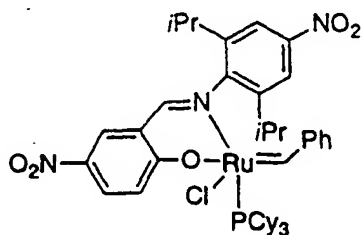
R¹¹ is an aryl or heteroaryl substituted with at least one electron
 withdrawing group. In especially preferred embodiments, R⁹ is phenyl
 substituted with at least one bulky substituent and at least one electron
 withdrawing group, and R¹¹ is phenyl substituted with at least one electron
 15 withdrawing group. Suitable examples of electron withdrawing groups include
 but are not limited to: halide, C₁-C₁₀ alkyl substituted with one or more halides,
 and nitro. Suitable examples of bulky substituents include but are not limited to
 tertiary C₃-C₁₀ alkyl and aryl.

20 Two of the most preferred embodiments of the present invention include:



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and



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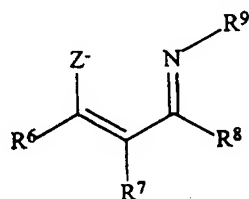
In addition to being valuable in their own right, the chelate structure of the inventive Schiff base compounds provide a sufficiently rigid structure for the design of chiral and/or cis/trans-selective metathesis catalysts. For example, depending on the nature of the reaction, it may be desirable to have the catalyst be chiral or prochiral. Illustrative uses of such compounds include the kinetic resolution of chiral olefins and asymmetric induction in prochiral triene ring closing reactions. Cis/trans-selectivity may be achieved by controlling the steric bulk of the ligands to influence the relative energies of the reaction intermediates that lead to different products.

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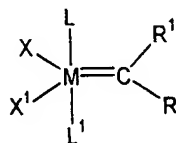
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In another embodiment of the present invention, methods for preparing the Schiff base complexes are presented. In general the method reacting a salt of a Schiff base of the general formula

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with a catalyst of the general formula

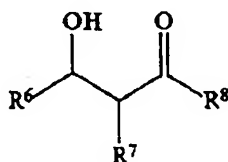


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wherein M, R, R¹, R⁶, R⁷, R⁸, R⁹, X, X¹, L and L¹ are as previously defined.

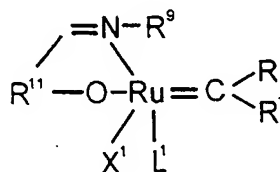
Although any salt may be formed, thallium salts were found to be particularly effective.

In preferred embodiments, the Schiff base is formed from the condensation of
 5 an aldehyde or a ketone of the general formula



with an amine of the general formula H_2NR^9 .

In more preferred embodiments, the condensation reaction is between an
 10 aldehyde, $\text{R}^{11}(\text{HC}=\text{O})(\text{OH})$, and an amine, H_2NR^9 , to yield catalysts of the general formula



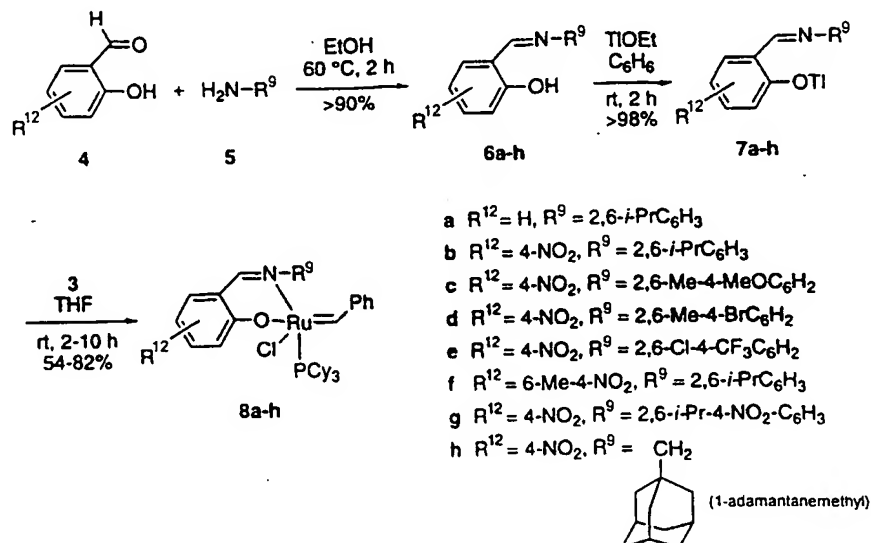
wherein X^1 , L^1 , R , R^1 , R^9 , and R^{11} are as previously described. Particularly preferred aldehydes include substituted and unsubstituted salicylaldehyde.

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For the purposes of clarity, the synthesis of the Schiff base derivatives of ruthenium and osmium catalysts will be illustrated with reference to specific catalyst embodiments, ruthenium complex 2 or 3. However, it should be understood that the forthcoming methods are generally applicable.

20

Scheme 1



As illustrated by Scheme 1, salicylaldimine ligands **6a-h** were prepared by simple condensation of salicylaldehydes **4** and aliphatic or aromatic amine derivatives **5** in excellent yields. The salicylaldimine ligands were quantitatively converted to the corresponding thallium salts upon treatment with thallium ethoxide. The resulting Schiff base ligands were substituted for X and L ligands in complex **2** or **3**.

The efficiency of the substitution reactions to yield the desired Schiff base catalysts **8a-h** varied depending on the bulk of the substituents on the ligands. For example, while thallium salts of ligands bearing a methyl group (**7f**) on the 6-position of the phenoxy part readily underwent substitution with **2** or **3**, the reaction of ligands bearing bulkier substituents (*i.e.*, *t*-Bu group) on the same position gave poor conversion under various substitution conditions. Reaction of **3** with ligands derived from anilines having number 2- and 6-substituents produced multiple complexes. However, presumably due to the steric reasons, ligands bearing highly bulky groups (*i.e.*, triisopropylsilyloxy-) on the 2- and 6-

positions of benzimine exhibited relatively very poor reactivity in the reaction with 3. Nevertheless, the Schiff base ligand substitution described above is surprisingly robust and allows for the synthesis of a diverse set of Schiff base catalysts.

5

Despite the quantitative conversion (by NMR) of 3 to the Schiff base ruthenium complexes in all cases, isolated recrystallization yields were lower due to the high solubility of the product complexes in most organic solvents. The ruthenium Schiff base benzyldiene species **8a-h** are very stable solids to air or moisture, and in some cases, can be further purified by column chromatography using silica gel. Moreover, the complexes show negligible amounts of decomposition in solution (CH_2Cl_2 or C_6H_6), even when heated at temperatures as high as 85 °C. For example, as shown by Table 1, although ruthenium complex 3 (a representative example of a previously described ruthenium metathesis catalysts) decomposed significantly after only 30 minutes at 85 °C, inventive complex **8b** was virtually unaffected.

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Table 1. Comparisons of Catalyst Decomposition Rates

	complex 3	complex 8b
Initial concentration	4.2 mmols	4.0 mmols
30 minutes at 85°	1.3 mmols	3.6 mmols
60 minutes at 85°	0.6 mmols	3.8 mmols

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As it will be explained in greater detail below, the unexpected increase in thermal stability of these catalysts over the previously described ruthenium and osmium metathesis catalysts makes them much more amenable to industrial applications.

25

Structural Characterization of the Schiff Base Substituted Ruthenium Complexes.

Substitution of one phosphine and one chloride ligand with a Schiff base ligand

was unambiguously indicated by characteristic NMR spectral changes for all substitution reactions (7 → 8, Scheme 1). The coupling constants between the carbene proton H_a and the coordinated phosphine has been found to be sensitive to the relative orientation of the plane defined by the atoms of the carbene fragment and that of the P-Ru-P plane. When the carbene plane is 90° to the P-Ru-P plane, $J_{\text{PH}} = 0$ and $J_{\text{PH}} > 10$ when they are coplanar.

In contrast to complex 3 (singlet, 20.1 ppm in CD₂Cl₂), the chemical shifts of the benzyldiene proton in the compounds 8a-h appear between 19.8 and 18.7 ppm as doublet (Table 2). As expected, the complexes bearing ligands with more electron withdrawing substituents were shifted to more downfield. Proton-phosphorous couplings also varied depending on the nature of the Schiff base ligands. Especially noteworthy is that coupling constants J_{PH} are more sensitive to the steric bulk rather than electronic contribution of the substituents on the Schiff base ligands. This suggest that although the ligand coordination around the ruthenium metal center is similar, the relative geometry of each species varies slightly depending on the steric demands caused by the ligands. For instance, while sterically crowded ligands give lower JPH coupling constants (*i.e.*, 2.7 Hz in 8f), those values increase upon reduction of steric demands in the Schiff bases (*i.e.*, 4.8 Hz in 8d). As found in the proton NMR spectroscopy, the ³¹P spectra for the coordinated phosphine ligands in 8a-h are also dependent on the electronic nature of the Schiff base ligands. For instance, while chemical shift of phosphorus is in the range of 51-54 ppm for aniline derived ligands, it is shifted to upfield (39 ppm) for 8h.

**Table 2. NMR Data for Ruthium Carbene Complexes
8a-8h and J (in Hz, CD_2Cl_2)**

entry	compound	$^1H\alpha$	J_{HP}	^{31}P
1	8a	19.68	3.6	52.23
2	8b	19.77	3.3	52.23
3	8c	19.49	4.7	50.51
4	8d	19.48	4.8	50.62
5	8e	19.39	4.5	50.65
6	8f	19.69	2.7	53.50
7	8g	19.72	3.3	52.54
8	8h	18.68	13.5	38.95

5 Representative of complexes **8a-h**, the structure of the Schiff base substituted
benzylidene species **8b** was further confirmed by a single crystal X-ray analysis.
The crystals suitable for X-ray structure determination were isolated from
concentrated diisopropyl ether solution at -20 °C. The data collection and
refinement data of the analysis is summarized in Table 3 and selected bond
10 distances and angles are listed in Table 4.

Table 3. Summary of Crystal Data and Structure Refinements of 8b.

Empirical formula	C ₄₄ H ₆₀ ClN ₂ O ₃ PRu·0.31 CH ₂ Cl ₂ ·0.17 H ₂ O
Formula weight	863.53
Crystal system	Prismatic Monoclinic (dark brown)
Space group	P2 ₁ /c (#14)
Temperature	160 K
Unit cell dimensions	$a = 9.123 (4) \text{ \AA}$ $b = 24.320 (7) \text{ \AA}$ $c = 19.863 (5) \text{ \AA}$
Z	4
Volume	4405 (3) Å ³
μ	5.30 cm ⁻¹ ($\mu_{\text{max}} = 0.13$)
2 Θ	3 - 5°
Crystal size (mm)	0.10 x 0.13 x 0.44
Reflections measured	17106
Independent reflections	7741
Goodness-of-fit on F ²	1.64 for 658 parameters and 7741 reflections
Final R indices [F _o]	0.079 for 5735 reflections with F _o ² > 2 σ (F _o ²)
Final weighted R [F _o ²]	0.121 for 7741 reflections

**Table 4. Selected Bond Lengths (Å) and Angles (deg)
for Ruthenium Complex 8b**

Bond Lengths (Å)			
Ru-Cl	1.85 (6)	P-C33	1.860 (6)
Ru-O1	2.055 (4)	P-C39	1.862 (6)
Ru-N1	2.106 (4)	O1-C20	1.288 (9)
Ru-P	2.345 (2)	N1-C8	1.473 (7)
Ru-Cl	2.382 (2)	N1-C14	1.301 (7)
C1-C2	1.451 (8)	C14-C15	1.433 (8)
P-C27	1.864 (7)	C1-H1 (Carbene H)	0.94 (6)
Bond Angles (degree)			
C1-Ru-O1	98.1 (2)	C8-N1-Ru	121.5 (3)
C1-Ru-N1	103.5 (2)	C33-P-Ru	114.2 (2)
O1-Ru-N1	88.9 (2)	C39-P-Ru	117.5 (2)
C1-Ru-P	96.8 (2)	C27-P-Ru	102.4 (2)
O1-Ru-P	88.4 (1)	C33-P-C39	11.7 (3)
N1-Ru-P	159.8 (1)	C33-P-C27	103.9 (3)
C1-Ru-Cl	88.7 (2)	C33-P-C27	105.2 (3)
O1-Ru-Cl	173.0 (1)	O1-C20-C15	124.7 (5)
P-Ru-Cl	89.0 (1)	N1-C14-C15	129.4 (5)
Ru-Cl-H1	113.1 (36)	C2-C1-H1	111.6 (36)

5

10

In the solid state, the molecule adopts a distorted trigonal bipyramidal coordination geometry. The bulky 2,6-diisopropyl benzimine occupies an axial position *trans* to the tricyclohexyl phosphine and the phenoxy part is positioned at an equatorial position with a nearly linear O1-Ru-Cl angle (173.0°). The two aromatic rings of the Schiff base ligand are positioned with respect to each other at a 80.1° angle. While the benzyldiene moiety in complex 3 is perpendicular to the P1-Ru-P2 plane, the angle of the carbene unit in the structure of **8b** to the

P-Ru-N1 plane is 87.14°. This distortion of the carbene plane is consistent with the nonzero value of J_{PH} for **8b**. The Ru-Cl (carbene carbon) bond distance [1.850(6) Å] are similar to those in related compounds;

5 RuCl₂(=CHCH=CPh₂)PCy₃ [$d(\text{Ru-C})$, 1.851(21) Å], [RuCl(=C(OMe)-(CH=CPh₂)(CO)(*Pi*-Pr₃)₂)] [BF₄] [$d(\text{Ru-C})$, 1.874(3) Å] or RuCl₂(=CH-*p*-C₆H₄Cl)(PCy₃)₂ [$d(\text{Ru-C})$, 1.838(3) Å].

Use of the Schiff base Derivatives in Metathesis Reactions

10 The inventive Schiff base catalysts may be used for any metathesis reaction. In general, methods for performing metathesis reactions comprise contacting at least one of the inventive catalyst with an olefin. Practice of the present invention may occur either in the presence or absence of solvents. In solventless reactions, the inventive catalysts typically dissolve in the olefin being reacted. As used herein, the term "olefin" is an unsubstituted or substituted

15 hydrocarbon with at least one carbon-carbon double bond. The hydrocarbon may be straight-chain, branched, or a cyclic compound. Illustrative examples of hydrocarbon substituents include but are not limited to: C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀

20 alkylthio, C₁-C₂₀ alkylsulfonyl, C₁-C₂₀ alkylsulfinyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

25 One particularly important metathesis reactions is ring opening metathesis polymerization ("ROMP") of cyclic olefins. Illustrative examples of cyclic olefins for ROMP include but are not limited to norbornene, cyclobutene, norbornadiene, cyclopentene, dicyclopentadiene, cycloheptene, cyclooctene, 7-oxanorbornene, 7-oxanorbornadiene, cyclooctadiene, and cyclododecene.

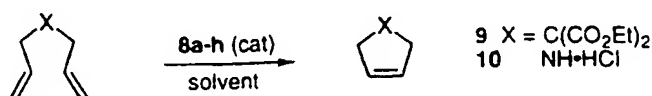
30 Another important metathesis reaction is is ring closing metathesis ("RCM"). In RCM, a non-cyclic diene (an olefin having two carbon-carbon double bonds) is

contacted with at least one of the inventive catalysts to form a cyclic olefin. Although the inventive catalysts may be used in any metathesis reaction, the use in RCM reactions is particularly preferred because it is favored over competing reactions at higher temperatures.

5

Scheme 2 illustrates the use of the Schiff base ruthenium carbene complexes 8a-h in an RCM reaction.

Scheme 2



In general, the inventive compounds tend to be less reactive at room temperature than the previously described ruthenium and osmium carbene complexes. However, *the reactivity increases dramatically at higher temperature*. For instance, although the ring closure of diethyl diallylmalonate ester 9 proceeds in 12 hour at room temperature with complex 8g (8 mol%, CH₂Cl₂), the reaction is completed in 1 hour at 70°C with the same carbene catalyst (3 mol%, C₆H₆). In another example, the use of complex 8b results in nearly 100% yield when the reaction is carried at 55°C with no evidence of catalyst decomposition even after 2 days at that temperature. This high product yield is a surprising and unexpected result because of the number of competing pathways for diene reactants.

20

The pronounced difference in reactivities between room and elevated temperatures poses several advantages to the industrial use of these catalysts. For example, the use of the Schiff base catalysts of the present invention presents an elegant and simple method for controlling the pot life (which is the time during which the monomer/catalyst mixture may be worked on) of the polymerization reaction mixture. Relying on the temperature dependent

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kinetics of the polymerization reaction, all the pre-polymerization steps for making a molded part (*i.e* mixing the olefin monomer with catalyst, casting/injecting/pouring the reaction mixture into a mold) can occur at room temperature. Since the inventive catalysts are not very active at this
5 temperature, the preparatory steps can occur without fear of premature polymerization. Once the reaction is ready to proceed, the mixture can be heated to the necessary temperature to allow the polymerization reaction to occur at the desired rate. Suitable temperatures will depend on the specific inventive catalyst. However, the elevated temperature is typically at least about
10 40°C.

In another example, the catalysts of the present invention may be used for the formation large molded products. The polymerization of thick parts has been particularly problematic because the exothermic nature of the reaction tended to
15 kill the previously described metathesis catalysts during the course of the polymerization reaction. As a result, polymerization of these products tended to be uneven with the centers of thick regions being especially susceptible to incomplete polymerization. In contrast, because of their increased thermal stability, such problems may be avoided with the use of the inventive catalyst .

20 Yet another feature of the catalysts of the present invention is their ability to retain catalytic activity even in polar protic solvents. The use of polar protic solvents is necessary particularly when a desired substrate is not soluble in common nonpolar solvents. For example, diallylamine·HCl salt **10** which is not
25 soluble in common nonpolar solvents was cleanly cyclized in methyl alcohol with complex **8a** (5 mol%, 40 °C, 12 h).

In summary, the Schiff base derivatives of ruthenium and osmium complexes are important catalysts in their own right exhibiting high thermal stability and
30 high metathesis activity (even in polar protic solvents). In addition, because they provide convenient routes for including additional functionalities, Schiff

base derivatives may play a key role in the design of chiral or cis/trans-selective olefin metathesis catalysts.

5

Experimental Section

Unless otherwise noted, all operations were carried out using standard Schlenk techniques or dry-box procedures. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres dry-box. ¹H-NMR (300.1 MHz) and ¹³C-NMR (75.49 MHz) spectra were recorded on a General Electric QE-300 spectrometer. ³¹P-NMR (161.9 MHz) spectra were recorded on a JEOL GX-400 spectrometer. NMR Chemical shifts are reported in ppm downfield from tetramethylsilane ("TMS") (δ scale) with TMS employed as the internal solvent for proton spectra and phosphoric acid employed as the internal solvent for phosphorous spectra. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside). Analytical thin-layer chromatography ("TLC") was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All solvents were rigorously degassed in 18 L reservoirs and passed through two sequential purification columns. Complex 3 and 2,6-dimethyl-4-methoxyaniline were prepared according to published procedures (Nguyen *et al.*, *J. Am. Chem. Soc.* **115**: 9858-9859 (1993); Sone *et al.*, *Nippon Kagaku Kaishi* **7** 1237-1240 (1982)). Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Company and used as received.

30

General Procedure for Preparation of Schiff base (6a-h).

The condensation of salicylaldehydes with aliphatic or aromatic amine derivatives were carried out with stirring in ethyl alcohol at 80°C for 2 hours.

Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture.

The solid was filtered, washed with cold ethyl alcohol and then dried *in vacuo* to afford the desired salicyladimine ligand in excellent yields. Any modifications are described for each reaction.

5

Schiff base 6a ($R^1 = H$, $R^2 = 2,6\text{-}i\text{-PrC}_6\text{H}_3$):

Salicylaldehyde (0.37 g, 3.0 mmol), 2,6-diisopropylaniline (0.53 g, 3.0 mmol) and ethanol (15 mL) afforded 0.76 g (90%) of the title compound as a yellow solid. A drop of formic acid was used to accelerate the condensation reaction.

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mp. 60-61°C; $^1\text{H-NMR}$ (CDCl_3) δ 13.16 (s, 1H), 8.34 (s, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.22 (bs, 3H), 7.10 (d, $J = 8.4$ Hz, 1H), 6.99 (t, $J = 7.5$ Hz, 1H), 3.20 (septet, $J = 6.6$ Hz, 2H), 1.20 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (CDCl_3) δ 166.4, 161.0, 145.9, 138.4, 133.0, 132.0, 125.3, 123.0, 118.8, 118.4, 117.1, 27.9, 23.3; HRMS (EI) for $\text{C}_{19}\text{H}_{23}\text{NO}$ $[\text{M}]^+$ 281.1780, found 281.1786.

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Schiff base 6b ($R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-}i\text{-PrC}_6\text{H}_3$):

5-Nitrosalicylaldehyde (1.10 g, 6.60 mmol), 2,6-diisopropylaniline (1.20 g, 6.60 mmol) and ethanol (25 mL) afforded 2.0 g (93%) of the title compound as a yellow solid. mp. 122-124°C; $^1\text{H-NMR}$ (CDCl_3) δ 14.35 (s, 1H), 8.43 (s, 1H), 8.38 (d, $J = 2.7$ Hz, 1H), 8.32 (d, $J = 9.3$ Hz, 1H), 7.25 (bs, 3H), 7.15 (d, $J = 9.0$ Hz, 1H), 2.97 (septet, $J = 6.9$ Hz, 2H), 1.22 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (CDCl_3) δ 166.8, 165.2, 144.4, 139.7, 138.4, 128.3, 128.2, 126.1, 123.3, 118.3, 117.3, 28.1, 23.3; HRMS (CI) for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 327.1709, found 327.1708.

20

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Schiff base 6c ($R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-Me-4-MeOC}_6\text{H}_2$):

5-nitrosalicylaldehyde (6.68 g, 40 mmol), 2,6-dimethyl-4-methoxyaniline (6.65 g, 44 mmol) and ethanol (140 mL) afforded 11.52 g (96%) of the title compound as a yellow solid. mp. 122-124°C; $^1\text{H-NMR}$ (CDCl_3) δ 14.67 (s, 1H), 8.41 (s, 1H), 8.33 (d, $J = 2.7$ Hz, 1H), 8.28 (dd, $J = 9.1, 2.7$ Hz, 1H), 7.10

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(d, $J = 9.1$ Hz, 1H), 6.68 (s, 2H), 3.81 (s, 3H), 2.24 (s, 6H); $^{13}\text{C-NMR}$ (CDCl_3) δ 167.6, 165.0, 157.3, 130.2, 128.3, 128.2, 118.5, 117.5, 113.9, 55.4, 18.9; HRMS (CI) for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 301.1188, found 301.1196.

5 Schiff base 6d ($\text{R}^1 = 4\text{-NO}_2$, $\text{R}^2 = 2,6\text{-Me-4-BrC}_6\text{H}_2$):
 5-Nitrosalicylaldehyde (0.67 g, 4.0 mmol), 4-bromo-2,6-dimethylaniline (0.80 g, 4.0 mmol) and ethanol (15 mL) afforded 1.41 g (91%) of the title compound as a yellow solid. mp. 194-196°C; $^1\text{H-NMR}$ (CDCl_3) δ 13.96 (s, 1H), 8.41 (s, 1H), 8.35 (d, $J = 2.7$ Hz, 1H), 8.30 (d, $J = 9.0$ Hz, 1H), 7.28 (s, 2H), 7.13 (d, $J =$
 10 9.0 Hz, 1H), 2.19 (s, 6H); $^{13}\text{C-NMR}$ (CDCl_3) δ 166.4, 165.5, 145.6, 139.8, 131.0, 130.2, 128.4, 128.2, 118.5, 118.2, 117.3, 18.1; MS (CI) 350 (100), 348 (92), 268 (29), 131 (91), 104 (25), 77 (29).

Schiff base 6e ($\text{R}^1 = 4\text{-NO}_2$, $\text{R}^2 = 2,6\text{-Cl-4-CF}_3\text{C}_6\text{H}_2$):
 15 5-Nitrosalicylaldehyde (1.30 g, 8.0 mmol), 4-amino-3,5-dichlorobenzotrifluoride (1.80 g, 8.0 mmol) and ethanol (25 mL) afforded 2.70 g (90%) of the title compound as a yellow solid. mp. 173-174°C; $^1\text{H-NMR}$ (CDCl_3) δ 12.96 (s, 1H), 8.68 (s, 1H), 8.43 (d, $J = 2.7$ Hz, 1H), 8.36 (dd, $J = 9.3$, 2.7 Hz, 1H), 7.70 (s, 2H), 7.17 (d, $J = 9.3$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3) δ 168.7,
 20 166.1, 145.7, 140.1, 129.4, 129.1, 127.6, 125.8, 125.7, 118.5, 116.9; HRMS (CI) calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3\text{F}_3\text{Cl}_2$ $[\text{M}+\text{H}]^+$ 378.9864, found 378.9866.

Schiff base 6f ($\text{R}^1 = 6\text{-Me-4-NO}_2$, $\text{R}^2 = 2,6\text{-i-PrC}_6\text{H}_2$):
 25 3-Methyl-5-nitrosalicylaldehyde (0.63 g, 3.40 mmol), 2,6-diisopropylaniline (0.80 g, 3.40 mmol) and ethanol (20 mL) afforded 1.10 g (95%) of the title compound as a yellow solid. mp. 120-121°C; $^1\text{H-NMR}$ (CDCl_3) δ 14.50 (s, 1H), 8.38 (s, 1H), 8.21 (s, 1H), 7.23 (s, 4H), 2.95 (septet, $J = 6.9$ Hz, 2H), 2.42 (s, 3H), 1.20 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (CDCl_3) δ 165.4, 144.4, 139.1, 138.5, 132.9, 128.5, 128.2, 126.0, 125.9, 123.2, 116.3, 28.0, 23.3, 15.4; HRMS
 30 (DCI) $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 341.1865, found 341.1873.

Schiff base 6g ($R^1 = 4\text{-NO}_2$, $R^2 = 2,6\text{-}i\text{-Pr-4-NO}_2\text{-C}_6\text{H}_3$):

5-Nitrosalicylaldehyde (1.0 g, 6.0 mmol), 2,6-diisopropyl-4-nitroaniline (1.30 g, 6.0 mmol) and ethanol (20 mL) afforded 2.0 g (91%) of the title compound as a yellow solid. mp. 118-120°C; $^1\text{H-NMR}$ (CDCl_3) δ 13.34 (s, 1H), 8.43 (s, 2H), 8.33 (dd, $J = 9.0, 2.4$ Hz, 1H), 8.09 (s, 2H), 7.18 (d, $J = 9.0$ Hz, 1H), 3.00 (septet, $J = 6.9$ Hz, 2H), 1.23 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (CDCl_3) δ 166.0, 165.7, 150.3, 145.8, 140.3, 134.0, 128.8, 128.6, 118.9, 118.1, 117.1, 28.3, 22.6; HRMS (DCI) $\text{C}_{19}\text{H}_{22}\text{N}_3\text{O}_5$, $[\text{M}+\text{H}]^+$ 372.1559, found 372.1560.

Schiff base 6h ($R^1 = 4\text{-NO}_2$, $R^2 = 1\text{-adamantanemethyl}$):

5-Nitrosalicylaldehyde (0.84 g, 5.0 mmol), 1-adamantanemethylaniline (0.90 g, 5.0 mmol) and ethanol (15 mL) afforded 1.40 g (92%) of the title compound as a yellow solid. mp. 178-180°C; $^1\text{H-NMR}$ (CDCl_3) δ 15.18 (s, 1H), 8.21 (s, 1H), 8.16 (t, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.3$ Hz, 1H), 3.29 (s, 2H), 2.00 (s, 3H), 1.65 (m, 6H), 1.55 (bs, 6H); $^{13}\text{C-NMR}$ (CDCl_3) 172.9, 164.4, 137.2, 129.1, 128.5, 120.4, 115.1, 68.4, 40.1, 33.9, 27.9; HRMS (DCI) $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3$, $[\text{M}+\text{H}]^+$ 315.1709, found 315.1710.

General Procedure for the Preparation of Thallium Salts (7a-h).

To a solution of the appropriate Schiff base (6a-h) in benzene or THF (10 mL), a solution of thallium ethoxide in benzene or THF (5 mL) was added dropwise at room temperature. Using a glass pipette, the solution of thallium ethoxide in benzene or THF was filtered through a plug of glasswool to remove any impurities. Immediately after the addition, a pale yellow solid formed and the reaction mixture was stirred for 2 hour at room temperature. Filtration of the solid under a nitrogen or argon atmosphere gave the respective thallium salt (7a-h) in quantitative yield. The salt was immediately used in the next step without further purification.

General Procedure for the Preparation of Schiff Base Substituted Ruthenium Complexes (8a-h).

A solution of the appropriate thallium salt (7a-h) in THF (5 mL) was added to a solution of ruthenium complex 3 in THF (5 mL). The reaction mixture was stirred at room temperature for 3 hours. After evaporation of the solvent, the residue was dissolved in a minimal amount of benzene and cooled to 0°C. The thallium chloride (the byproduct of the reaction) was removed *via* filtration. The desired complex was then washed with cold benzene (10 mL x 3) and the filtrate was evaporated. The solid residue was recrystallized from pentane (-70°C) to give the respective Schiff base substituted ruthenium complex (8a-h) in moderate to good yield as a brown solid. Any modifications are described below for each reaction.

Ruthenium Schiff base Complex 8a:

Ruthenium complex 3 (1.20 g, 1.50 mmol), thallium salt 7a (0.78 g, 1.60 mmol), and THF (20 mL) afforded 0.89 g (75%) of the title complex as a brown solid. mp. 119-122°C; ¹H-NMR (CD₂Cl₂) δ 19.68 (d, *J* = 3.6 Hz, 1H), 8.06 (d, *J* = 5.4 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.33-7.00 (m, 8H), 6.60 (t, *J* = 7.2 Hz, 1H), 3.36 (septet, *J* = 6.9 Hz, 1H), 2.51 (q, *J* = 11.7 Hz, 3H), 2.13 (septet, *J* = 6.9 Hz, 1H), 1.79-1.52 (m, 20H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.22 (m, 10H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.75 (dd, *J* = 21.3, 6.9 Hz, 6H); ³¹P-NMR (CD₂Cl₂) δ 52.23; MS (FAB) 787 (3), 386 (12), 315 (26), 297 (19), 281 (49), 279 (19), 255 (8), 231 (20), 154 (23), 119 (23), 117 (100).

Ruthenium Schiff base Complex 8b:

Ruthenium complex 3 (1.65 g, 2.0 mmol), thallium salt 7b (1.10 g, 2.10 mmol), and THF (40 mL) afforded 1.40 g (82%) of the title complex as a brown solid. mp. 140-145°C; ¹H-NMR (CD₂Cl₂) δ 19.77 (d, *J* = 3.3 Hz, 1H), 8.27 (d, *J* = 2.7 Hz, 1H), 8.14 (d, *J* = 5.4 Hz, 1H), 8.10 (dd, *J* = 9.6, 2.7 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.21 (m, 2H), 7.09 (dd, *J* = 6.9, 1.8 Hz, 1H), 6.99 (d, *J* = 9.3 Hz, 1H), 3.26 (septet, *J* = 6.6 Hz,

1H), 2.52 (q, $J = 11.5$ Hz, 3H), 2.11 (septet, $J = 6.6$ Hz, 1H), 1.73 (bs, 20H), 1.40 (d, $J = 6.6$ Hz, 3H), 1.23 (m, 10H), 1.15 (d, $J = 6.9$ Hz, 3H), 0.78 (dd, $J = 17.4$, 6.9 Hz, 6H); ^{31}P -NMR (CD_2Cl_2) δ 52.23; HRMS (FAB) $\text{C}_{44}\text{H}_{60}\text{ClN}_2\text{O}_3\text{PRu}$ $[\text{M}]^+$ 832.3074, found 832.3104.

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Ruthenium Schiff base Complex 8c:

Ruthenium complex 3 (0.25 g, 0.30 mmol), thallium salt 7c (0.16 g, 0.32 mmol), and THF (3 mL) afforded 0.13 g (54%) of the title complex as a brown solid. mp. 139-142°C; ^1H -NMR (CD_2Cl_2) δ 19.49 (d, $J = 4.7$ Hz, 1H), 8.22 (d, $J = 2.8$ Hz, 1H), 8.08-8.04 (m, 3H), 7.98 (d, $J = 7.8$ Hz, 2H), 7.56 (d, $J = 7.4$ Hz, 1H), 7.35 (d, $J = 1.3$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 2H), 7.00 (d, $J = 9.6$ Hz, 1H), 3.79 (s, 3H), 2.38 (s, 6H), 1.75-1.21 (m, 30H); ^{31}P -NMR (CD_2Cl_2) δ 50.51; HRMS (FAB) $\text{C}_{41}\text{H}_{54}\text{ClN}_2\text{O}_4\text{PRu}$ $[\text{M}]^+$ 806.2553, found 806.2520.

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Ruthenium Schiff base Complex 8d:

Ruthenium complex 3 (0.41 g, 0.50 mmol), thallium salt 7d (0.32 g, 0.55 mmol), and THF (25 mL) afforded 0.35 g (80%) of the title complex as a brown solid. mp. 128-131°C; ^1H -NMR (CD_2Cl_2) δ 19.48 (d, $J = 4.8$ Hz, 1H), 8.22 (d, $J = 2.7$ Hz, 1H), 8.07 (dd, $J = 9.3$, 2.7 Hz, 1H), 8.03 (d, $J = 5.7$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.28 (t, $J = 7.8$ Hz, 2H), 7.17 (s, 1H), 7.00 (d, $J = 9.6$ Hz, 1H), 2.47 (q, $J = 12.0$ Hz, 3H), 2.37 (s, 3H), 1.78-1.63 (bs, 20H), 1.50 (d, $J = 13.5$ Hz, 3H), 1.30-1.16 (m, 10H); ^{31}P -NMR (CD_2Cl_2) δ 50.62; HRMS (FAB) $\text{C}_{40}\text{H}_{51}\text{BrClN}_2\text{O}_3\text{PRu}$ $[\text{M}]^+$ 856.1532, found 856.1573.

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Ruthenium Schiff base Complex 8e:

Ruthenium complex 3 (0.34 g, 0.40 mmol), thallium salt 7e (0.26 g, 0.44 mmol), and THF (20 mL) afforded 0.30 g (85%) of the title complex as a brown solid. mp. 145-149°C; ^1H -NMR (CD_2Cl_2) δ 19.39 (d, $J = 4.5$ Hz, 1H), 8.25 (d, $J = 2.7$ Hz, 1H), 8.09 (dd, $J = 9.3$, 2.7 Hz, 1H), 7.99 (m, 3H), 7.69 (d, $J = 18.0$ Hz, 1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.35 (s, 1H), 7.28 (t, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 9.6$ Hz, 1H), 2.48 (q, $J = 11.7$ Hz, 3H), 1.73-1.54 (m, 15H), 1.39 (m, 5H), 1.22

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(bs, 10H); ^{31}P -NMR (CD_2Cl_2) δ 50.65; HRMS (FAB) $\text{C}_{39}\text{H}_{45}\text{Cl}_3\text{F}_3\text{N}_2\text{O}_3\text{PRu}$ $[\text{M}]^+$ 886.1199, found 886.1179.

Ruthenium Schiff base Complex 8f:

5 Ruthenium complex 3 (0.82 g, 1.0 mmol), thallium salt 7f (0.60 g, 1.10 mmol), and THF (35 mL) afforded 0.68 g (80%) of the title complex as a brown solid. mp. 155-158°C; ^1H -NMR (CD_2Cl_2) δ 19.69 (d, $J = 2.7$ Hz, 1H), 8.11 (d, $J = 4.5$ Hz, 2H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.33 (s, 1H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.17 (m, 3H), 7.07 (d, $J = 7.2$ Hz, 1H), 3.22 (septet, $J = 6.6$ Hz, 1H), 2.58 (q, $J = 11.4$ Hz, 3H), 2.38 (s, 3H), 1.91 (septet, $J = 6.6$ Hz, 1H), 1.80-1.54 (m, 20H), 1.36 (d, $J = 6.6$ Hz, 3H), 1.19 (bs, 13H), 1.10 (d, $J = 6.6$ Hz, 3H), 0.85 (d, $J = 6.9$ Hz, 3H), 0.72 (d, $J = 6.3$ Hz, 3H); ^{31}P -NMR (CD_2Cl_2) δ 53.50; HRMS (FAB) $\text{C}_{45}\text{H}_{62}\text{ClN}_2\text{O}_3\text{PRu}$ $[\text{M}]^+$ 846.3230, found 846.3279.

15 Ruthenium Schiff base Complex 8g:

Ruthenium complex 3 (0.66 g, 0.80 mmol), thallium salt 7g (0.51 g, 0.88 mmol), and THF (50 mL) afforded 0.59 g (67%) of the title complex as a brown solid. mp. 160-163°C; ^1H -NMR (CD_2Cl_2) δ 19.72 (d, $J = 3.3$ Hz, 1H), 8.30 (d, $J = 2.7$ Hz, 1H), 8.13 (d, $J = 3.0$ Hz, 1H), 8.10 (s, 2H), 8.05 (d, $J = 2.1$ Hz, 1H), 7.95 (d, $J = 2.4$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.00 (d, $J = 9.6$ Hz, 1H), 3.29 (septet, $J = 6.6$ Hz, 1H), 2.48 (q, $J = 11.4$ Hz, 2H), 2.18 (septet, $J = 6.6$ Hz, 1H), 1.72 (bs, 20H), 1.45 (d, $J = 6.9$ Hz, 3H), 1.20 (m, 13H), 0.80 (dd, $J = 21.0, 6.6$ Hz, 6H); ^{31}P -NMR (CD_2Cl_2) δ 52.54; HRMS (FAB) $\text{C}_{44}\text{H}_{59}\text{ClN}_3\text{O}_3\text{PRu}$ $[\text{M}]^+$ 877.2924, found 877.2887.

25

Ruthenium Schiff base Complex 8h:

Ruthenium complex 3 (0.33 g, 0.40 mmol), thallium salt 7h (0.23 g, 0.44 mmol), and THF (20 mL) afforded 0.18 g (54%) of the title complex as a brown solid. mp. 162-166°C; ^1H -NMR (CD_2Cl_2) δ 18.68 (d, $J = 13.5$ Hz, 1H), 7.95 (dd, $J = 9.3$ Hz, 1H), 7.89 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 3.0$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 9.3$

30

Hz, 1H), 6.09 (d, $J = 10.8$ Hz, 1H), 3.00 (dd, $J = 10.8, 2.7$ Hz, 2H), 2.29 (q, $J = 11.4$ Hz, 3H), 1.99 (bs, 3H), 1.84 (bs, 3H), 1.73 (m, 20H), 1.57 (m, 10H), 1.25 (d, $J = 8.7$ Hz, 9H); ^{31}P -NMR (CD_2Cl_2) 38.95; HRMS (FAB) $\text{C}_{43}\text{H}_{60}\text{ClN}_2\text{O}_3\text{PRu}$ $[\text{M}]^+ 820.3074$, found 820.3079.

5

General Procedure for the Ring-Closing Metathesis of Diethyl Diallylmalonate using Ruthenium Schiff Base Catalysts 8a-h.

All reactions were performed on the benchtop in air by weighing 8 mol% of the respective catalyst (8a-h) into a dry NMR tube and dissolving the solid in 0.5 ml of CD_2Cl_2 or C_6D_6 . A solution of diethyl diallylmalonate (0.1 mmol) in CD_2Cl_2 or C_6D_6 (0.5 mL) was added. The tube was then capped, wrapped with parafilm, and shaken periodically. The studies were ran at both ambient temperatures and higher temperatures ($\sim 65^\circ\text{C}$) to access the activity and stability of the catalysts during the course of the reactions. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks.

10
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X-ray structure of the Ruthenium Complex 8b.

Crystals suitable for X-ray structure determination were grown from a solution of isopropyl ether at -20°C over a few days. The brown crystal used for data collection was 0.10 mm x 0.13 mm x 0.44 mm. Data collection was carried out at 160 K. A total of 17106 reflections were collected, 7741 of which were independent. Data collection parameters are summarized in part by the Table 2. The structure was solved by direct methods using the Siemens SHELXS-86 program. The molecule was refined isotropically (with riding H atoms on dichloromethane solvent) with a fractional population parameter for each solvent molecule also refined. The hydrogen atoms were originally placed at calculated positions. Eventually, the coordinates of all but two (H38a and H38b) were refined, with U_{iso} fixed at 1.2 times the U_{eq} of the attached atom. Refinement was full-matrix least-squares using SHELXL-93.

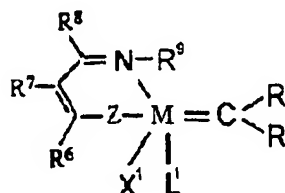
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Decomposition Experiment with Ruthenium Complexes 3 and 8b.

Two NMR tube samples were prepared in toluene-d₈, one containing 4.0 mmolar of 8b and the other containing 4.2 mmolar of 3, with an internal standard of anthracene. The samples were analyzed by ¹H-NMR and placed in an 85°C oil bath. After 30 minutes, the samples were again analyzed and replaced into the oil bath. After another 30 minutes, a final analysis by NMR was performed. For each analysis, the intensity of the carbene signal in the NMR was determined relative to the anthracene signal and used to calculate the molar concentration of the respective remaining carbene catalyst.

What is claimed is:

1. A compound of the general formula of the formula



5

wherein:

M is ruthenium or osmium;

X¹ is an anionic ligand;

10 L¹ is a neutral electron donor;

R and R¹ are each hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

Z is selected from the group consisting of oxygen, sulfur, -NR¹⁰, and -PR¹⁰, and

20 R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, each non-hydrogen group optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

25 wherein X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate,

and halogen.

2. The compound of claim 1 wherein

M is ruthenium;

5 R is hydrogen;

R¹ is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl;

L¹ is a phosphine of the formula PR³R⁴R⁵ wherein R³, R⁴, and R⁵ are each selected from the group consisting of aryl, C₁-C₁₀ primary alkyl, secondary
10 alkyl, and cycloalkyl; and,

X¹ is selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and, trifluoromethanesulfonate.

15 3. The compound as in claim 2 wherein:

X¹ is chloride;

L¹ is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R¹ is phenyl or vinyl, optionally substituted with one or more moieties
20 selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl;

R⁶ and R⁷ together form an aryl or heteroaryl group;

R⁸ is hydrogen; and,

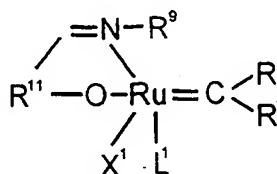
R⁹ is aryl or heteroaryl.

25 4. The compound as in claim 3 wherein

R⁶ and R⁷ together forms a phenyl group; and,

R⁹ is phenyl.

30 5. A compound of the formula



5

wherein:

X^1 is an anionic ligand;

L^1 is a neutral electron donor;

10

R and R^1 are each hydrogen or a substituent selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxy carbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, and aryl;

15

R^9 is selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, aryl, and heteroaryl, the non-hydrogen groups optionally substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, and aryl; and,

20

R^{11} is an aryl or heteroaryl, optionally substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, and aryl;

25

wherein X^1 , L^1 , R , R^1 , R^9 , and R^{11} each optionally includes one or more functional groups selected from the group consisting hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

6. The compound as in claim 5 wherein

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X^1 is selected from the group consisting of halide, CF_3CO_2 , CH_3CO_2 , CFH_2CO_2 , $(\text{CH}_3)_3\text{CO}$, $(\text{CF}_3)_2(\text{CH}_3)\text{CO}$, $(\text{CF}_3)(\text{CH}_3)_2\text{CO}$, PhO , MeO , EtO ,

tosylate, mesylate, and, trifluoromethanesulfonate;

L^1 is a phosphine of the formula $PR^3R^4R^5$ where R^3 , R^4 , and R^5 are each selected from the group consisting of aryl, C_1 - C_{10} primary alkyl, secondary alkyl, and cycloalkyl;

5 R is hydrogen; and,

R^1 is selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, and aryl.

7. The compound as in claim 6 wherein

10 X^1 is chloride;

L^1 is selected from the group consisting of $-P(\text{cyclohexyl})_3$, $-P(\text{cyclopentyl})_3$, $-P(\text{isopropyl})_3$; and $-P(\text{phenyl})_3$;

R^1 is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C_1 - C_5 alkyl, C_1 - C_5 alkoxy, and phenyl;
15 and,

R^9 and R^{11} are each aryl or heteroaryl.

8. The compound as in claim 7 wherein

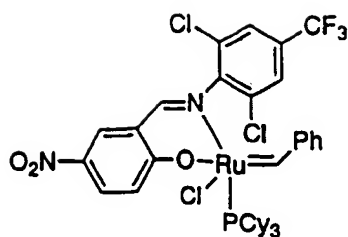
R^9 and R^{11} are each phenyl.

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9. The compound as in claim 7 wherein R^9 and R^{11} are both phenyl substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, and aryl, the R^9 and R^{11} groups each optionally including one or more functional groups selected from the
25 group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

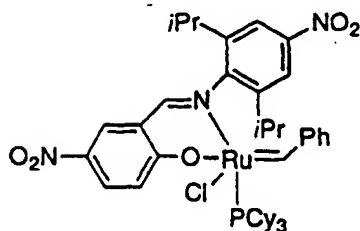
10. The compound as in claim 9 having the formula

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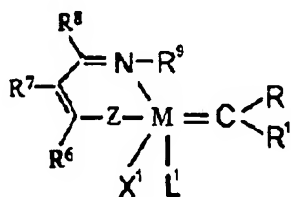
or



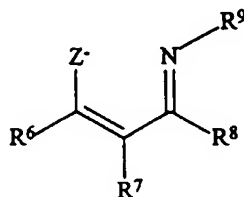
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11. A method for preparing a catalyst having the formula

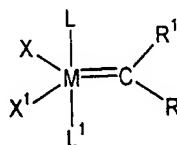


comprising contacting a salt of a Schiff base having the formula



with compound having the formula

20



5 wherein:

M is ruthenium or osmium;

X and X¹ are each an anionic ligand;

L and L¹ are each a neutral electron donor;

10 R and R¹ are each hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

15 Z is selected from the group consisting of oxygen, sulfur, -NR¹⁰, and -PR¹⁰, and

20 R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, each non-hydrogen group optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

25 wherein X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

12. The method as in claim 11 wherein the salt of the Schiff base is a thallium salt.

30 13. The method as in claim 12 wherein
M is ruthenium;

R is hydrogen;

R¹ is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl;

5 L and L¹ are each a phosphine of the formula PR³R⁴R⁵ where R³, R⁴, and R⁵ are each selected from the group consisting of aryl, C₁-C₁₀ primary alkyl, secondary alkyl, and cycloalkyl; and,

X and X¹ are each selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and, trifluoromethanesulfonate.

10

14. The compound as in claim 13 wherein:

X and X¹ are each chloride;

L and L¹ are each selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃; and -P(phenyl)₃;

15 R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl;

R⁶ and R⁷ together form an aryl or heteroaryl group;

R⁸ is hydrogen; and,

R⁹ is aryl or heteroaryl.

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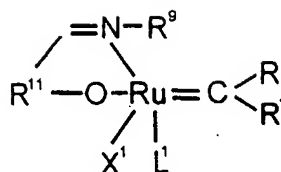
15. The compound as in claim 14 wherein

R⁶ and R⁷ together forms a phenyl group; and,

R⁹ is phenyl.

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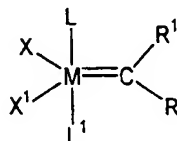
16. A method of preparing a catalyst having the formula



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comprising contacting a salt a Schiff base having the formula $\text{R}^{11}(\text{HC}=\text{NR}^9)(\text{O}^-)$ with a compound having the formula

10



wherein:

15

X and X¹ are each an anionic ligand;

L and L¹ are each a neutral electron donor;

20

R and R¹ are each hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

25

R⁹ is selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, the non-hydrogen groups optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl; and,

30

R¹¹ is an aryl or heteroaryl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl,

wherein X¹, L¹, R, R¹, R⁹, and R¹¹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol,

thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

5 17. The method as in claim 16 wherein the salt of the Schiff base is a thallium salt.

18. The method as in claim 16 wherein

X and X¹ are each selected from the group consisting of halide, CF₃CO₂,
10 CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and, trifluoromethanesulfonate;

L and L¹ are each a phosphine of the formula PR³R⁴R⁵ where R³, R⁴, and R⁵ are each aryl, C₁-C₁₀ primary alkyl, secondary alkyl, or cycloalkyl;

R is hydrogen; and,

15 R¹ is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl.

19. The method as in claim 18 wherein

X and X¹ are each chloride;

20 L and L¹ are each -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl; and

R⁹ and R¹¹ are each aryl or heteroaryl.

25

20. The method as in claim 19 wherein

R⁹ and R¹¹ are each phenyl.

21. The method as in claim 19 wherein R⁹ and R¹¹ are both phenyl

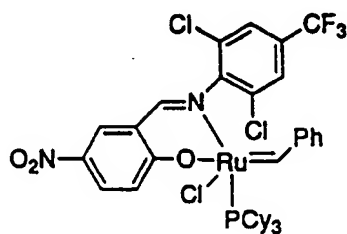
30 substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl; the R⁹ and R¹¹ groups each optionally

including one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

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22. The method as in claim 21 wherein the catalyst has the formula

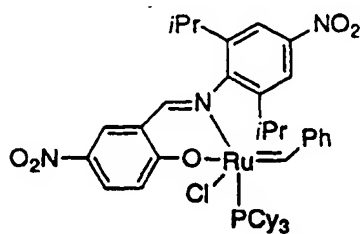
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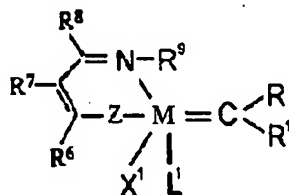
or

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23. A method for performing a metathesis reaction comprising contacting an olefin with a catalyst having the formula

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wherein:

M is ruthenium or osmium;

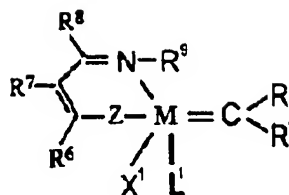
X¹ is an anionic ligand;

L¹ is a neutral electron donor;

- 5 R and R¹ are each hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties
- 10 selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;
- Z is selected from the group consisting of oxygen, sulfur, -NR¹⁰, and -PR¹⁰, and
- R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, each non-hydrogen group
- 15 optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;
- wherein X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic
- 20 acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

24. The method as in claim 23 wherein the olefin is a cyclic olefin.

- 25 25. A method for molding articles comprising
- (i) adding to a mold at room temperature an olefin and a catalyst having the formula



wherein:

M is ruthenium or osmium;

5 X¹ is an anionic ligand;

L¹ is a neutral electron donor;

R and R¹ are each hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

Z is selected from the group consisting of oxygen, sulfur, -NR¹⁰, and -PR¹⁰, and

15 R⁶, R⁷, R⁸, R⁹, and R¹⁰ are each selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, aryl, and heteroaryl, each non-hydrogen group optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl;

20 wherein X¹, L¹, Z, R, R¹, R⁶, R⁷, R⁸, and R⁹ each optionally includes one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen and

(ii) bringing the mold to a temperature of at least 40 °C.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23259

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07F 9/00, 15/00; C08F 4/80, 32/00

US CL :556/20, 21, 137; 526/93, 171, 283, 305, 306, 309, 941

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 556/20, 137

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, REGISTRY and CA databases

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,312,940 A (GRUBBS et al.) 17 May 1994, see entire document.	1-24
A,P	US 5,710,298 A (GRUBBS et al.) 20 January 1998, see entire document.	1-24
A,P	US 5,831,108 A (GRUBBS et al.) 03 November 1998, see entire document.	1-24
X,P	CHANG et al., Synthesis and Characterization of New Ruthenium-Based Olefin Metathesis Catalysts Coordinated with Bidentate Schiff-base Ligands. Organometallics, 03 August 1998, Vol. 17, No. 16, pages 3460-3465, especially pages 3461 and 2465.	1-24

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

22 FEBRUARY 1999

Date of mailing of the international search report

02 MAR 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23259

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,E	US 5,840,820 A (DESIMONE et al.) 24 November 1998, column 3, line 21 through column 9, line 31.	1-25